Solid source growth of graphene with Ni–Cu catalysts: towards high quality in situ graphene on silicon

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Abstract
We obtain a monolayer graphene on epitaxial silicon carbide on silicon substrates via solid source growth mediated by a thin Ni–Cu alloy. Raman spectroscopy consistently shows an \( I_D/I_G \) band ratio as low as \( \sim 0.2 \), indicating that the graphene obtained through this method is to-date the best quality monolayer grown on epitaxial silicon carbide films on silicon. We describe the key steps behind the graphene synthesis on the basis of extensive physical, chemical and morphological analyses. We conclude that (1) the oxidation, amorphisation and silicidation of the silicon carbide surface mediated by the Ni, (2) the liquid-phase epitaxial growth of graphene as well as (3) the self-limiting graphitization provided the molten Cu catalyst, are key characteristics of this novel synthesis method.

Keywords: graphene, 3C–SiC, silicon, liquid phase growth, soft x-rays

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(Some figures may appear in colour only in the online journal)
used to obtain high quality, scalable graphene for industrial applications. Of both methods, CVD growth on metal substrates has been commonly used to produce large-area, high-quality monolayer graphene. However, the graphene needs to be transferred onto a semiconducting or insulating substrate which degrades the electrical and mechanical performance of devices. To address this issue, researchers have proposed direct growth of graphene on semiconducting surfaces such as germanium (Ge) layer on silicon (Si) wafers [7, 8]. Although a high-quality monolayer graphene is obtained in this case, the weak adhesion between the graphene and the underlying Ge layer is a serious drawback for the fabrication of functional devices.

On the other hand, growth via thermal decomposition of bulk silicon carbide (SiC) at high temperature (1300–1700 °C) provides the most promising pathway towards clean, structurally coherent and mechanically reliable epitaxial graphene at the wafer scale [6, 9, 10]. However, SiC substrates are very expensive, difficult to micro-machine and available in relatively small size (150 mm) as compared to silicon wafers (300–450 mm) [11, 12]. Growth of graphene on hetero-epitaxial cubic silicon carbide (3C–SiC) films grown on low-cost silicon (Si) substrates has been explored to address these issues [13–15]. Graphene growth on 3C–SiC/Si substrates offers compatibility with established Si fabrication technologies, allowing for seamless integration with a large number of electronic and opto-electronic technologies. Although the thermal decomposition of 3C–SiC on Si to produce graphene appears promising for large-scale production of graphene-based electronic devices, it has been mostly limited to the use of 3C–SiC(111) oriented surfaces [15–17]. The quality of the graphene produced via this method is limited by the high defect densities of hetero-epitaxially grown SiC on silicon, and difficulty in controlling the Si sublimation rates in high/ultrahigh vacuum at relatively low (1100–1300 °C) temperatures [16, 18].

In parallel, several research groups have investigated a catalyst-based method for obtaining graphene on the 3C–SiC surface [19–21]. This method involves depositing a thin nickel film on the SiC surface and subsequently annealing the sample at temperatures ranging from 750 °C to 1200 °C; a temperature much lower than that for the sublimation process. However, the quality of the graphene formed is often found to be strongly non-uniform. In most cases graphene was observed to grow on the metal surface and so required transfer to a semiconductor or an insulating surface to obtain a functional device. This transfer requirement hinders its utility for large-scale device fabrication [19, 21].

We have recently pioneered an alternative, alloy-mediated approach for direct and self-aligned synthesis of high quality graphene on 3C–SiC/Si [22, 23]. In this process, the carbon is supplied from the solid-phase using thin epitaxial SiC films on Si as the source. In contrast with the thermal decomposition based route, our alloy-mediated graphitization takes place at comparatively moderate temperatures (900–1100 °C) and moderate vacuum (∼10⁻⁴ mbar). The graphene obtained exhibits a high adhesion energy with the underlying SiC substrate [22], estimated to be about an order of magnitude higher than that of graphene transferred onto a SiO₂ layer on Si [24]. Furthermore, this solid-source alloy-mediated approach benefits from straightforward wafer-level patterning capabilities and warrants a more detailed understanding of its synthesis mechanisms. It is anticipated that both the Ni–Cu alloy and the residual partial pressure of oxygen in the vacuum chamber play a crucial catalytic role, affecting the uniformity and quality of the graphene layer. Herein we focus on the mechanism of alloy-mediated graphene growth on 3C–SiC on Si (100) substrates. We identify the oxidation and amorphization of the SiC as important intermediate steps of the solid-source graphitization, and the key role of the Cu catalyst component, responsible for an efficient and self-limiting process.

2. Experimental

2.1. Sample preparation

Hetero-epitaxial 3C–SiC films, 250 nm thick, were grown on 150 mm diameter Si(100) wafers in a hot-wall horizontal low pressure CVD reactor through alternate supply epitaxy comprised of SiH₄ and C₂H₂ at 1000 °C and a carbonization process at 950 °C [25]. The 3C–SiC/Si wafers were then diced into 10 mm × 10 mm samples for further experiments and characterization.

Following growth of the SiC, either a single layer of nickel or double layer of nickel and copper were sputtered on the 3C–SiC surface. For the nickel growth, Ni (99.99%) was deposited via Ar⁺ ion DC magnetron sputtering (Surrey Nano Systems) at 100 °C and a base pressure of 10⁻⁸ mbar with thicknesses of ∼5, 8, 11 and 14 nm. For the double layer growth, an additional layer of ∼15 nm copper, Cu (99.95%) was deposited on top of the Ni layer using a DC Ar⁺ ion sputtering system (EMITECH K575X) with a deposition current of 100 mA at a base pressure of 10⁻⁴ mbar. The alloy-mediated graphitization was performed in a high temperature, low vacuum tube furnace (Carbolite HT tube furnace), evacuated to a pressure below 5 × 10⁻⁴ mbar. The samples were heated and maintained at 1100 °C for 75 min and left to cool to room temperature under vacuum. A highly intermixed layer of unreacted metal, metal silicides and excess carbon is produced during the graphitization process, which was then selectively removed by immersing the samples in a wet etch solution (Freckle etch) [23] for 20 h, followed by rinsing with Milli-Q water. All subsequent characterizations were performed after the removal of this intermixed layer.

2.2. Sample characterization

In order to characterize the quality of the graphene grown on the sample surfaces, Raman spectroscopy was performed at room temperature in a backscattering geometry using a Renishaw InVia spectrometer operating at 514.5 nm (argon–ion laser) with a spot size of approximately 1 µm². For calibration, we used a silicon reference sample producing a standard peak at ∼520.5 cm⁻¹ [26]. The D, G and 2D bands in the Raman spectrum of the graphene layers were monitored and the intensity ratio of the D- and G-bands (I_D/I_G) was calculated. In order
to improve the statistical accuracy of the \( I_D/I_G \) ratio, Raman spectra were recorded at five different sites (at the centre as well as the four corners) on each 10 mm × 10 mm sample. In addition, confocal Raman mapping was performed using a WITec ALPHA300 RA CRM/AFM operating at 532 nm laser (1 mW power measured before the objective). The scan size, step size, number of points and integration time were 40 \( \mu m \) × 40 \( \mu m \), 0.25 \( \mu m \), 25 600 and 0.75 s respectively.

Atomic force microscopy (AFM) was performed in non-contact mode using a Park NX20 atomic force microscopy system over 5 × 5 and 1 × 1 \( \mu m^2 \) scan areas with 512 × 512 pixel resolution.

High-resolution transmission electron microscopy (HRTEM) of the graphene/3C–SiC/Si sample was performed using an FEI Cs-corrected Titan3 microscope operating at 80 keV. Cross-sectional TEM specimens (sample foils) were prepared via a focused ion beam (FIB) lift-out technique using a FEI Strata DB235 FIB/SEM with a Ga\textsuperscript{+} ion source. The foils were excavated from the bulk samples and thinned to about 500 nm. Subsequently, Ar\textsuperscript{+} ion milling was conducted in a Fiscione NanoMill\textsuperscript{™} to remove Ga\textsuperscript{+} ion damage. A 2 \( \mu m \) thick Pt/Au protective layer was deposited onto the samples prior to FIB milling.

The chemical composition and elemental depth profile of the graphene/3C–SiC/Si layered system was characterized using multiple techniques. Time-of-flight secondary-ion mass spectrometry (ToF-SIMS) was performed using an ION-ToF GmbH TOF-SIMS 5 instrument. Data was acquired from a 100 \( \mu m \) × 100 \( \mu m \) area using a 30 keV Bi\textsuperscript{3+} pulsed primary-ion beam, whilst sputtering a 300 \( \mu m \) × 300 \( \mu m \) area centered at the same location with 2 keV Cs\textsuperscript{+} ions. ToF-SIMS profile showed that nearly 650 s is required to etch the entire 250 nm SiC film. Therefore, the etch rate was calculated around \( \approx 23 \text{ nm min}^{-1} \). The base pressure during the acquisition was 3 × 10\textsuperscript{−10} mbar.

X-ray photoelectron spectroscopy (XPS) was employed for depth profiling the elemental composition of the graphitized sample. The samples were initially sputter etched and characterized using a laboratory-based XPS instrument, Kratos AXIS Nova x-ray photoelectron spectrometer (Kratos Analytical Ltd) equipped with a monochromated Al K\( \alpha \) x-ray source (\( h\nu = 1486.6 \text{ eV} \)) operating at 150 W. Spectra were recorded over a binding-energy range of 0–1300 eV, at a pass energy of 160 eV, while sputtering a 3 mm × 3 mm area with 1 keV Ar\textsuperscript{+} ions (target current 0.1–0.2 \( \mu A \)). Spectral acquisitions were limited to a 110 \( \mu m \) × 110 \( \mu m \) area at the centre of the sputtered region. Prior to sputtering, the pressure in the analysis chamber was 2.6 × 10\textsuperscript{−9} mbar. The sputter-etch rate was calculated by measuring the actual crater depth using optical profilometry. The crater depth was measured to be \( \approx 110 \text{ nm} \), corresponds to a sputter rate of \( \approx 2.8 \text{ Å min}^{-1} \).

Complementary synchrotron-based XPS measurements were performed at the soft x-ray beamline at the Australian Synchrotron. Samples were introduced into the ultra-high vacuum system at the beamline and annealed at 200 °C for several hours in order to remove airborne contaminants and ensure a pristine surface. Following this, the XPS measurements were performed using a SPECS Phoibos 150 hemispherical analyser, operating at a pass energy of 10 eV. Detailed C 1s and Si 2p core levels were measured at 150 eV, 350 eV, 850 eV, and finally 1486.6 eV; by tuning the photon energy in this way, the photoelectron mean free path within the material was systematically changed allowing for variation in the sampling depth of the XPS measurement without the need for sputtering the sample.

3. Results

3.1. Raman spectroscopy

Figure 1(a) compares the Raman \( I_D/I_G \) band ratios (intensity ratio of the D- and G-bands) of the graphene grown on 3C–SiC films on Si (1 0 0) substrates using a Ni layer only, with those obtained using a Ni/Cu double layer. Note that the thickness of the Cu layer remained constant (~15 nm) when the Ni/Cu double layer is used. The error bar represents the standard deviation of the \( I_D/I_G \) ratios, measured at five different sites over the 10 mm × 10 mm graphene samples. Data obtained from samples produced over more than 10 experimental runs fell within the displayed error bars. The average \( I_D/I_G \) ratio of the graphene grown using only a Ni layer varies between

![Graphene/SiC (100) (NiCu) Graphene/SiC (100) (Ni only)](image)
0.6 and 1. This ratio drops to about 0.2–0.3 when graphene is grown using the Ni and Cu layers. These results confirm our recent findings [22] that an additional Cu layer deposited on top of the Ni film significantly improves the graphene quality. Note that the \( I_D/I_G \) ratio shown in table 1 (0.24 ± 0.05) is considerably lower than our previously reported values (0.5–0.8) [22, 23], thanks to an improved control of the graphitization process.

We selected a sample prepared under the conditions which yielded the lowest \( I_D/I_G \) ratio (8 nm Ni/15 nm Cu) for further characterization. The \( I_D/I_G \) ratio along with the peak position and full width half maximum (FWHM) of the G and 2D peak of the corresponding sample are reported in table 1.

Figure 1(b) shows the Raman spectra of the selected sample, indicating the D, G and 2D bands at ~1355, 1585 and 2707 cm\(^{-1} \), respectively. The G band is located at ~1585 cm\(^{-1} \) with a FWHM of about ~25 cm\(^{-1} \). The position of G band is very similar to that for graphene on a bulk SiC surface (1586 cm\(^{-1} \); FWHM <30 cm\(^{-1} \)), as reported in table 1. The intensity of the 2D band is slightly higher than the G band, indicating the presence of monolayer graphene [27].

Previous studies [28, 29] have reported that exfoliated monolayer graphene exhibits a relatively narrow and intense 2D band (FWHM <30 cm\(^{-1} \)) at ~2678 cm\(^{-1} \). Figure 1(c) shows that the 2D band of our graphene sample is symmetrical and fitted well using a single Lorentzian peak centered at 2707 cm\(^{-1} \) with a FWHM of ~40 cm\(^{-1} \) (table 1), consistent with the characteristics of a monolayer graphene. However, in comparison to exfoliated graphene, the 2D band of our sample is significantly shifted towards higher frequency by approximately 30 cm\(^{-1} \). This blue shift could be related either to electron/ hole doping or the strain induced by the substrate [28, 30]. As the dependence on doping of the 2D band shift is very weak [31], the significant blue shift of the 2D band of our samples is likely a consequence of a compressive thermal strain induced in the graphene upon cooling [28, 32]. Note that the Raman spectra acquired on the graphene/3C–SiC sample (figure 1(b)) is remarkably consistent over the entire 10 mm × 10 mm surface.

Additionally, a confocal Raman mapping was performed, measuring 25 600 points over a 40 µm × 40 µm area (see supplementary information, figure S1 (stacks.iop.org/JPhysD/50/095302/mmedia)). The average \( I_D/I_G \) ratio, \( I_{2D}/I_G \) ratio and 2D FWHM is calculated as ~0.4, ~1 and ~45 cm\(^{-1} \) respectively (table 1), the latter figures both suggesting the prevalence of monolayer graphene distributed over the surface. Note that the intensity ratio of 2D to G band alone would be a weak indication of single layer as reported by Tiberj et al [36]. To confirm the number of graphene layers, the sample is further characterized with the help of HRTEM, ToF-SIMS and soft x-ray photoelectron spectroscopy. Although the \( I_D/I_G \) values calculated herein do not yet match those corresponding to the best quality CVD graphene or graphene grown on bulk SiC via thermal decomposition [5, 10], they represent the highest quality graphene grown on 3C–SiC/Si reported to date [14, 16, 34, 35]. For example, Fukidome et al reported average \( I_D/I_G \) values as low as ~0.4 for graphene grown on 3C–SiC(11 1)/Si(1 1 0), however, multilayer graphene (6–7 layers) was observed in their experiments [15]. In addition, the crystallite size (\( L_a \)) calculated using the expression [37]

\[
L_a (nm) = (2.4 \times 10^{-10})\lambda_{laser}^2 (I_D/I_G)^{-1} (\lambda = 514.5 \text{ nm in this work})
\]

indicates an average graphene domain size of around 35–60 nm, considerably larger than the crystallite size \( L_a = 10–15 \text{ nm} \) reported for the graphene grown on 3C–SiC on Si via thermal decomposition method [16]. Therefore this catalytic alloy approach yields to-date the best quality, large area graphene grown in situ on 3C–SiC films on silicon wafers.

3.2. Transmission electron microscopy (TEM) and low energy electron diffraction (LEED)

Figure 2(a) shows the dark-field cross-sectional TEM micrograph of the graphene/3C–SiC sample. The top dark layer is the protective gold and platinum material deposited prior to FIB preparation of the TEM cross sections. The middle lighter contrast region corresponds to a diffuse TEM diffraction pattern (not shown here), consistent with an amorphous material approximately 20 nm thick. However, complementary LEED measurements performed on this surface (figures 2(b) and (c)) reveal a clear square symmetry pattern with a high background. Since LEED is extremely surface sensitive (a few atomic layers at most) [38], this result indicates that regions of ordered crystalline symmetry exist at the surface (at least within the sampling depth of the LEED). These regions exhibit the same four-fold rotation symmetry as the 3C–SiC.
surface. The TEM image also shows an atomic sheet resting above this ~20 nm thick amorphous layer, underneath the protective layer. This sheet is most certainly the monolayer graphene, which is further confirmed by investigating chemical profile of the top few nm of the surface in following sections. Towards the bottom of the image, the single crystalline 3C–SiC(1 0 0) film is observed, characterized by the presence of typical stacking faults travelling along the (1 1 1) planes [25].

3.3. Time of flight secondary ion mass spectrometry (ToF-SIMS)

Changes in the chemical composition as a function of depth for the selected graphene/3C–SiC sample (table 1) were investigated with ToF-SIMS depth profiling (figure 3). The figure plots the intensity (normalized to maximum) of the C⁺, Si⁺, SiC⁺ and Cs₂O⁺ secondary ion mass fragments as a function of depth, from the surface, through the graphene layer, and into the 3C–SiC layer underneath. Note that Cs₂O⁺ is formed by association of any oxygen atoms present in the sample with Cs⁺ ions from the sputter source and allows oxygen, which normally ionizes with a negative charge, to be profiled simultaneously with the positively charged C⁺, Si⁺, and SiC⁺ ions.

Since the sample surfaces can be contaminated with adventitious hydrocarbons from atmospheric exposure, data from top ~1 nm is eliminated from the profile. A marked decrease in the C⁺ ions intensity over the next ~1 nm of the profile probably attributed to the monolayer graphene at the surface. It appears from the Cs₂O⁺ profile that there is extensive oxidation of the SiC layer down to a depth of ~20 nm. This thickness corresponds well with the amorphous region observed using TEM between the graphene and the pristine 3C–SiC layers in figure 2(a). A relatively constant SiC⁺ signal is also obtained from the surface to a depth of around 30 nm. It is important to note that these ions can be generated from either pure SiC or oxidized SiC (oxycarbide), supplementary the hypothesis of the existence of crystalline SiC grains in an amorphous oxidised region, as observed in the TEM and LEED images (figure 2).

3.4. X-ray photoelectron spectroscopy (XPS) depth profiling

Seeking further insight into the nature of the amorphous region beneath the graphene, we have undertaken additional chemical depth profiling using x-ray photoelectron spectroscopy (XPS), performed using two XPS methodologies. Figure 4 shows an ion-etched XPS depth profile taken from a laboratory-based XPS instrument (Kratos AXIS Nova x-ray photoelectron spectrometer), extending from the surface, through the graphene (indicated by the sharp peak in the C profile at the top surface) and into the 3C–SiC film. The elemental profiles reveal once again a significant amount of oxygen (>10 atomic %) present in the top ~20 nm of the sample along with carbon and silicon, indicative of an oxidized top region. This oxygen profile again corresponds roughly to the total thickness of the amorphous region observed with TEM in figure 2(a). In particular, we note that the top ~5 nm of the surface just underneath the graphene contains up to 35% oxygen, indicating a region largely depleted of carbon and containing potentially various oxidation states of silicon. Importantly, in the inset of the TEM image in figure 2(a), a lighter-contrast amorphous layer about ~5 nm thick can be distinguished just underneath the graphene. Lighter contrast possibly indicates
lower density and/or lower carbon content, which agrees with the information from the XPS profile.

3.5. Synchrotron XPS results

Figures 5(a)–(c) show the Si 2p core level photoemission spectra of the sample measured at three different photon energies: 150 eV, 350 eV and 850 eV respectively. Note that as the photon energy is lowered, the mean free path of the photoelectrons becomes smaller, and thus the signal becomes more surface sensitive [39]. The approximate total sampling depths for individual photon energy are indicated in the figure 5. Each spectrum is deconvoluted into four Voigt doublets by a standard peak fitting routine [40–42] and the respective fitting parameters are summarized in the Supplementary Information (figure S2 and table S1). For clarity, only the Si 2p$_{3/2}$ components are displayed. The binding energies, Gaussian and Lorentzian widths used for fitting are consistent with previous literature [40–42]. At 150 eV incident photon energy (figure 5(a)), a dominant peak is seen at ~101 eV, which can be attributed to Si 2p$_{3/2}$ from pure SiC [43]. A clear peak resolved at ~101.6 eV, indicating the presence of either the silicon suboxide Si$^{1+}$ (in the form of Si$_2$O) [41], the oxy carbide SiO$_C$$_3$ [40, 44] or a mixture of both (the expected peak positions for these two environments are so close as to be not resolved here). Two comparatively weaker components corresponding to Si$^{2+}$ (SiO)/Si–O–C and Si$^{3+}$ (SiO$_2$) can also be seen at binding energies of ~102.3 eV and ~103.5 eV respectively. The results obtained here are in good agreement with the XPS results of Seyller et al [40] and Virojanadara et al [45], on the thermal oxidation of the 4H–SiC(1 1 2 0) surface. Figures 5(b) and (c) shows that these higher binding energy components decrease relative to the pure SiC signal as the incident photon energy, and therefore the total sampling depth, increases. Therefore, they can be associated with the surface region only. At 350 eV (figure 5(b)), the SiO$_2$ component has almost disappeared, however the SiO$_C$$^3$/Si$_2$O and Si$^{2+}$/Si–O–C components can still be observed, indicating that the silica is a superficial oxide located right at the surface. Again, this is in agreement with the results reported by Seyller et al [40]. At the highest incident photon energy (850 eV), the Si$^{2+}$/Si–O–C component becomes negligible, with only the SiO$_C$$^3$/Si$_2$O component evident along with the SiC component. This suggests that the SiO$_C$$^3$/Si$_2$O component is buried beneath the Si$^{2+}$/Si–O–C layer and extends to a greater depth. It is important to note that for all three photon energies, pure SiC is the most dominant component, even for the most surface sensitive energy of 150 eV where the oxide components still represent a small fraction of the signal. Given the sampling depth at 150 eV is around ~2 nm, and that from the earlier ToF-SIMS and TEM measurements a ~20 nm thick amorphous oxygen-containing surface region was observed, one cannot conclude a simple model of a pure ~20 nm oxidized SiC layer on top of a pristine SiC. Instead, these results suggest a mixed phase of crystalline SiC and amorphous oxidized SiC exhibiting a non-abrupt concentration gradient away from the surface.

Aforementioned results are consistent when we examine the carbon core level, where C1s spectra were measured at 350 eV, 850 eV and 1486.6 eV incident photon energies (maintaining approximately the same sampling depth as the silicon data) as shown in figures 5(d)–(f) respectively. At 350 eV incident photon energy (figure 5(d)) (the most surface sensitive), a dominant peak due to sp$^2$-bonded carbon atoms is observed at ~284.5 eV along with that corresponding to pure SiC (~283.3 eV). The XPS curve fitting has also resolved three additional oxide-related peaks centered at 283.7 eV, 285.05 eV and 285.76 eV, indicative of the presence of SiO$_C$$_3$, Si–O–C and C–O/C/Si–O–Si [40, 42, 44] respectively. The SiO$_C$$_3$ is an amorphous metastable phase [44] composed of Si$^{1+}$, Si$^{2+}$ and Si$^{3+}$ components. Although the relative concentration of
each component of SiOC could not be determined, the prominent SiOC3 and Si\(^2+\)/SiO\(^-\)-C peaks present in the Si 2p core level spectra (figure 5(a)) indicate the predominance of the Si1+ and Si 2+ components, respectively. The best fit parameters including peak type, peak position, Lorentzian width and Gaussian width for each component are presented in the supplementary information (table S2). Figures 5(e) and (f) shows the intensity of the sp2 carbon peak relative to the SiC component reduces significantly when the incident photon energy is increased indicating the graphene contribution is confined to the SiC surface only as expected. The SiO\(^-\)-C and SiO\(^-\)-Si/C\(^-\)-O\(^-\)-C components also seem confined to the topmost part of the sample surface and start reducing relative to the SiC with an increase in the incident photon energy. However, the intensity of the SiO\(^x\)C\(^y\) component is almost constant relative to the SiC signal as the photon energy increases, confirming the oxidation of deeper SiC layers as observed in TEM, ToF-SIMS and XPS depth profiles. As with the Si 2p data, the pure SiC signal is quite prominent at all times; this component again supports the idea of pure SiC crystallites contained within the amorphous oxidized film.

Finally, to determine the amount of metal (Ni and Cu) residues in the sample, we performed a XPS survey scans (figure S3). We noticed that the wet etch procedure was successful in removing any Ni or Cu residues completely from the sample surface.

4. Discussion (graphitization mechanism)

Considering the data presented in the preceding sections, we outline a model for the graphitization mechanism, accounting for the formation of monolayer graphene on top of a highly oxidized and amorphous region of the SiC layer. A full schematic describing the model is shown in figure 6.

We propose that the complete graphitization process includes the following main stages: (1) oxidation of Ni, (2) amorphization and oxidation of the top SiC layer, releasing carbon in the intermixed layer (3) graphene layer formation.

4.1. Oxidation of Ni

At low temperature (~400 °C), Ni starts reacting with the ambient oxygen present in the furnace forming Ni(II) oxide [46]. XPS evidence of which was reported in our previous work [22].

4.2. Amorphization, oxidation of SiC and release of carbon

In the temperature range of 400 °C–750 °C, Ni/NiO assists in weakening the Si–C bonds and starts diffusing into the crystalline 3C–SiC film [47]. Above ~750 °C, the Ni/NiO possibly reacts with SiC forming amorphous SiO\(^x\)C\(^y\) material and NiSi\(_2\) while also releasing atomic carbon [19, 48]. XPS evidence for the presence of NiSi\(_2\) before etching away the intermixed layer (NiSi\(_2\)+Ni + Cu + atomic carbon) is reported in the
Figure 6. Schematic of the proposed alloy-mediated catalytic graphitization mechanism. (a) Double layer of Ni and Cu sputtered on the 3C–SiC surface. (b) Annealing the Cu/Ni/3C–SiC sample at 1100 °C leads to the formation of graphene layer on a ~20 nm thick oxidized SiC layer along with an intermixed layer on top. (c) The intermixed layer is removed by wet chemical etching and a graphene layer obtained directly on the 3C–SiC surface.

4.3. Graphene layer formation

Note that the graphitization process takes place at 1100 °C, however, the melting point of NiSi₂ and Cu is ~993 °C and ~1085 °C respectively [48], which means that the graphene growth takes place in the melt. Since the density of Cu (8.96 g cm⁻³) is higher than NiSi₂ (4.83 g cm⁻³) and Ni (8.90 g cm⁻³) [49], at 1100 °C, the liquid Cu will likely diffuse to the bottom of the intermixed layer, as shown in figure 6(b). This molten Cu would follow conformally the surface morphology of the 3C–SiC film, acting as a pseudo Cu foil for the growth of graphene. The atomic carbon present in the melt is most likely catalyzed into active carbon species by Cu and subsequently chemically adsorbed potentially on both its faces upon cooling (figure 6(b)). We expect that the graphene growth herein is self-limiting, producing monolayer graphene on both top and bottom surfaces of Cu, by analogy with the more established graphene growth on copper foil [5, 50]. The intermixed layer along with top graphene and Cu layer are finally removed using the wet etch (Freckle) solution leaving bottom single layer graphene on the SiC surface (figure 6(c)). Unfortunately, this alloy-mediated process also adds undesirable roughness to the sample. The root mean square roughness of the graphene/3C–SiC sample is found around ~9 nm, which is about twofold that of bare 3C–SiC films grown on silicon substrate (~4 nm) [11].

As the graphene is obtained by means of a liquid phase epitaxial process, the adatoms will benefit from longer diffusion lengths and thus more relaxed growth conditions as compared with the pure solid phase epitaxy when using thermal decomposition route. Overall, the nickel and the oxygen seem to play a key catalytic role in facilitating the release of C from SiC at relatively low temperatures, plus the presence of molten silicon enable a liquid phase epitaxy of graphene. Oxygen helps to accelerate the graphitization process as suggested in previous reports [51, 52]. The presence of copper is essential for making the graphene growth more uniform, self-limiting and controlled [23]. Note that, in addition, the catalytic action of the liquid Cu will not be hampered by grain boundaries typical in a solid Cu film/foil. Finally, we believe that the Cu is also critical for an even dilution of small amounts of nickel across large areas and for accelerating the graphitization process.

5. Conclusions

A solid-source, Ni–Cu alloy-mediated graphitization yields direct, in situ growth of a monolayer graphene on heteroepitaxial silicon carbide on silicon substrates. Raman spectroscopy consistently shows an \( \text{I}_D/\text{I}_G \) band ratio as low as ~0.2 over large areas, indicative of the best quality graphene grown on epitaxial silicon carbide on silicon wafers reported to-date. Physical and chemical analyses suggest that the graphitization process is very likely taking place in a melt condition and includes at least three intermediate stages: (1) oxidation of Ni, (2) oxidation (and corresponding depletion of carbon) and amorphization within the top few tens of nm of the SiC layer, accompanied by the release of atomic carbon, and (3) formation of the graphene layer on the surface of the SiC layer through the key catalytic action provided by the Cu. The synergistic combination of the catalytic actions of nickel and oxygen for releasing carbon from the silicon carbide, of nickel for the formation of silicides, and of copper for the self-limiting graphitization, leads to the formation of a monolayer graphene on 3C–SiC on silicon with superior uniformity and quality as compared to the use of more common thermal decomposition of 3C–SiC on Si.

The understanding of this novel approach to graphene growth and the avenues for its further improvement make it possible to finally envisage in situ, wafer-level graphene on silicon of suitable quality coating complex 2D and 3D micro/ nano structures for a variety of electrical, thermal, electronic and photonic applications on silicon.

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References

[5] Li X et al 2009 Science 324 1312